



Short communication

Nanocomposite polymer electrolyte membranes based on poly(vinylphosphonic acid)/sulfated nano-titania

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H I G H L I G H T S

- Nanocomposite electrolytes containing poly(vinylphosphonic acid) and sulfated nano-titania were prepared.
- The proton conductivity of PVPATS has been found to be $0.03 \text{ (S cm}^{-1}\text{)}$ at 150°C .
- As acid-modified oxide composite membranes, its conductivity, structural, and morphological investigation were done.

A R T I C L E I N F O

Article history:

Received 28 February 2012

Received in revised form

21 April 2012

Accepted 6 May 2012

Available online 5 June 2012

Keywords:

Nanocomposite polymer electrolyte
Proton conductivity

A B S T R A C T

Proton conductors comprising phosphonic acid units are very promising due to their oxidative stability as well as high proton conductivity. In the present work, the membrane materials were produced by mixing of poly(vinylphosphonic acid) (PVPA) with sulfated nano-titania at various concentrations to get PVPATS_x where *x* designates the molar ratio of the polymer repeating units to sulfate units (varied from 1 to 4). The structure of the nanocomposite polymer membrane is confirmed by FT-IR spectroscopy. The TGA results verify that the presence of sulfated nano-titania in the complex polymer electrolytes suppressed the formation of phosphonic acid anhydrides up to 200°C . DSC results indicate that the *T_g* of the materials shifts to higher temperatures as sulfated nano-titania content increases. In the anhydrous state, the proton conductivity of PVPATS is found to be $0.03 \text{ (S cm}^{-1}\text{)}$ at 150°C . Proton conductivity of these membranes are also measured and compared with previous studies. The results suggest that proton conduction is occurred between surface of the nano-titania particles with the aid of sulfonic acid and phosphonic acid units.

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1. Introduction

Great improvements have been made for the preparation and modification of polymer electrolyte membranes (PEMs). They are one of the key materials of proton exchange membrane fuel cells (PEMFCs) that transport protons from anode to cathode in fuel cells. One of the challenges in attaining optimum performance from PEMFCs is to achieve effective hydration of the ionomeric structure of the membrane. [1–4].

Recently, an increasing attention is presently being devoted to polymer nanocomposites due to the possibility of production of high proton conductive membranes that can be applied in PEMFCs. Numerous nanocomposites are known today where inorganic additives in the polymer nanocomposite membranes provide rigidity, thermal stability as well as mechanical stability [5]. In

earlier studies inorganic fillers such as TiO_2 and SiO_2 have been frequently used where these fillers are indeed effective in improving mechanical properties of the composite membranes [6–13]. The ionic conductivity of polymer membranes including metal oxides, i.e., TiO_2 , increases for a large temperature range.

The inorganic additive, TiO_2 is believed to be the most promising material at the present because of its powerful oxidation strength, high photostability, and nontoxicity [14,15]. Studies on Nafion/ TiO_2 composite membranes have attracted the attention of many research groups. Their results show that the morphological properties of the filler play a major role in the performance of the composite membranes at a high operating temperature [6,16–19].

The increase in the nanoparticles content in the polymer matrix, results in the decrease in proton conductivity. The reason can be attributed to low proton conductivity of the fillers which may also blocks the diffusion of the H^+ ions themselves. Embedding acid-functionalized fillers can potentially enhance or preserve proton conductivity, reduce methanol permeability and optimize the interfacial compatibility of the polymer electrolyte membranes

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[20–27]. In this context, as a new type of polymer nanocomposite membrane, acid-modified nanoparticles have been introduced into polymers improving the proton conductivity. Acid-modified oxides such as sulfated titania and zirconia have been proposed as super acids where ionic conductive groups exist on its solid surface [28,29]. Previously, Kanamura et al. have reported sulfuric acid-modified porous silica [30], and Miyayama et al. have reported a zirconia-based material [31]. These sulfated nanoparticles are expected to show the highest proton conductivity when they dispersed in the membranes.

Functional polymers including vinylphosphonic acid can be potential candidates as proton conducting membranes. High concentration of phosphonic acid groups which are bonded by hydrogen bridges can provide a suitable pathway for proton conduction. Poly (vinylphosphonic acid), PVPA is the best model matrix for the study of the structure and proton conduction mechanism [32–35].

In this paper, we report on novel proton conducting superacid nanocomposite polymer membranes. Sulfated nano-titania was synthesized by hydrolysis and precipitation of titanyl sulfate and the membrane materials were produced by complexation with PVPA at various molar ratio. The material production, proton conduction properties and thermal properties were investigated. The results are discussed in detail and compared with previously reported systems.

2. Experimental

2.1. Materials and preparation

Vinylphosphonic acid (>95%, Fluka) DMF, (>99%, Fluka) and α - α' -azodiisobutyramidine dihydrochloride (98%, Fluka) were used as received. PVPA was synthesized by free radical polymerization of vinylphosphonic acid [36].

Sulfated nano-titania was prepared according to following procedure have reported by Sakai et al. [37]. First, 5 g of titanyl sulfate ($\text{TiOSO}_4 \cdot n\text{H}_2\text{O}$, $n = 1\text{--}2$) was dissolved into 200 mL of water and stirred continuously for 40 min. The solution was then heated under continuous stirring, resulting in a white precipitate at around 70 °C. The white precipitate was collected by suction filtration, washed several times with distilled water, the resultant powder was stored in glove box [37]. The amount of sulfate groups in the sample powder was to be about $1 \times 10^{-3} \text{ mol g}^{-1}$ from the acid–base titration.

PVPA (Fig. 1) and sulfated nano-titania were mixed at various concentrations to get PVPATS_x where x designates the molar ratio of the polymer repeating unit to sulfate units and varied from 1 to 4 (Table 1). Then the mixture was further stirred under nitrogen atmosphere at 50 °C for 24 h, i.e., until getting a homogeneous milky solutions. The polymer films were cast onto polished PTFE

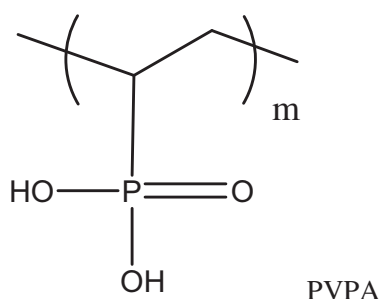


Fig. 1. Structure of PVPA.

Table 1

Max. proton conductivity and T_g (°C) values for the membranes.

Sample name	PVPA: TS (molar ratio)	T_g (°C)	Max. proton conductivity (S cm^{-1})
PVPATS	1:1	78 °C	0.03 (S cm^{-1}) at 150 °C
PVPATS ₂	1:2	82 °C	5×10^{-3} (S cm^{-1}) at 150 °C
PVPATS ₄	1:4	94 °C	0.01 (S cm^{-1}) at 150 °C

plates, dried under vacuum at 50 °C and then stored in a glove box. Hygroscopic and free standing films were obtained and the materials and were denoted as PVPATS_x.

2.2. Characterizations

The FT-IR spectra of the samples were recorded on a Bruker Alpha-P ATR spectrometer in the range 4000–400 cm^{-1} , with 4 cm^{-1} resolution.

2.2.1. SEM

The surface morphology of blend membranes was investigated by scanning electron microscopy (SEM, Philips XL30S-FEG). All of the samples were sputtered with gold for 150 s before SEM measurements.

2.2.2. Thermal measurements

Thermal stabilities of the complex polymer electrolytes were examined by thermogravimetry (TG) analysis with a Perkin Elmer STA 6000. The samples (~10 mg) were heated from room temperature to 750 °C under N_2 atmosphere at a heating rate of 10 °C min^{-1} .

Differential scanning calorimetry (DSC) data were obtained using Perkin Elmer JADE DSC instrument. The measurements were carried out at a rate of 10 °C min^{-1} under a nitrogen flow.

2.2.3. Conductivity measurements

The proton conductivity studies of the samples were performed using a Novocontrol dielectric impedance analyzer. The samples were sandwiched between platinum blocking electrodes and the conductivities were measured in the frequency range 1 Hz to 3 MHz at 10 °C intervals. The temperature between –100 and 250 °C was controlled with a Novocontrol cryosystem.

3. Results and discussions

3.1. Characterizations

Fig. 2 shows the FT-IR spectra of PVPATS_x nanocomposite membranes. The FT-IR spectrum of PVPA shows strong bands between 1040 and 910 cm^{-1} that belong to asymmetric stretching vibrations of the P–OH group. The peak at 1150 cm^{-1} corresponds to P=O stretching. Additionally, phosphonic acid units give rise to broad bands with medium intensity between 1700–1590 cm^{-1} and 2850–2750 cm^{-1} region. FT-IR spectra of sulfuric acid-modified nano-titania shows characteristic peaks around 1650 cm^{-1} and at 980–1250 cm^{-1} . The peaks at 980–1250 cm^{-1} was attributed to bidentate sulfate coordination on the titania surface (980–990, 1040, 1130–1150 and 1210–1230 cm^{-1}) [38–40]. These peaks are overlapped with the corresponding peaks of phosphonic acid units of host matrix and became more intense. The S=O vibration at 1393 cm^{-1} , can be clearly observed from the sample sulfated nano-titania [41]. The broad band between 3500 cm^{-1} –2500 cm^{-1} is the hydrogen bonding network which is necessary for proton conduction [42].

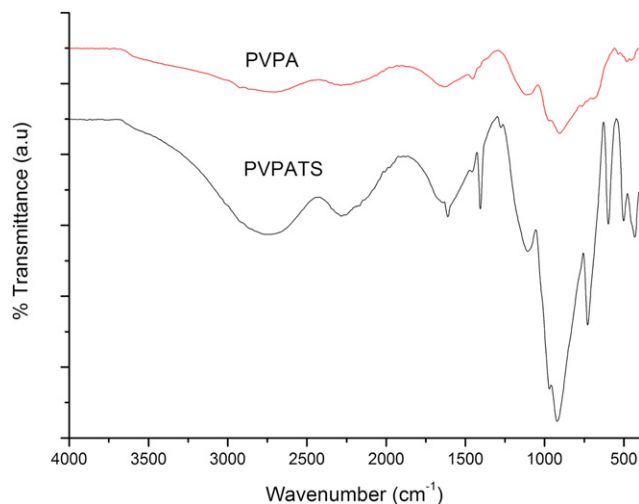


Fig. 2. FT-IR spectra of the PVPA and PVPATS composite membranes.

3.2. XRD

Phase investigation of the crystallized product was performed by XRD and the diffraction pattern is presented in Fig. 3. The XRD pattern indicates that the product is sulfated nano-titania, and the diffraction peaks are broadened owing to very small crystallite size which was approximately 10–15 nm according to Scherrer's equation. Similar results were reported in previous articles [37].

3.3. SEM

In order to examine the microstructures and nanofiller distribution within the nanocomposites, SEM analysis was conducted. Typical surface SEM photographs of PVPATS nanocomposite were illustrated in Fig. 4a) and b). From the figure, it was observed that sulfated nano-titania were homogeneously dispersed and embedded in the PVPA matrix. Such homogeneous distribution can be reason of complexation between PVPA and sulfated nano-titania. This result is also consistent with the DSC curves of the impregnated membranes that have no separate T_g transition.

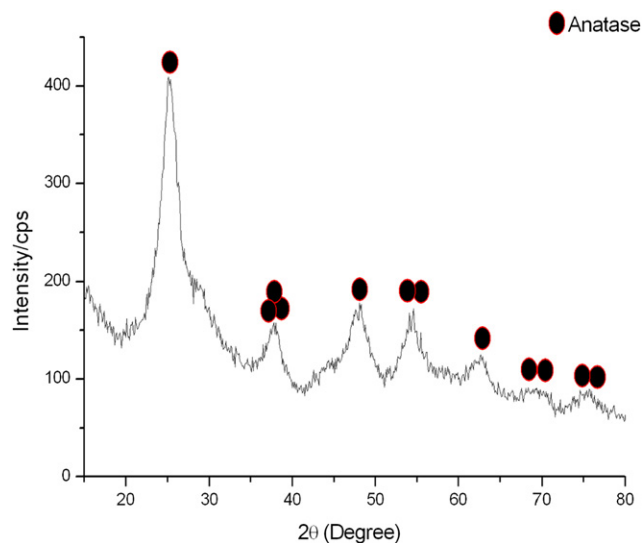


Fig. 3. XRD pattern of hydrous sulfated nano-titania.

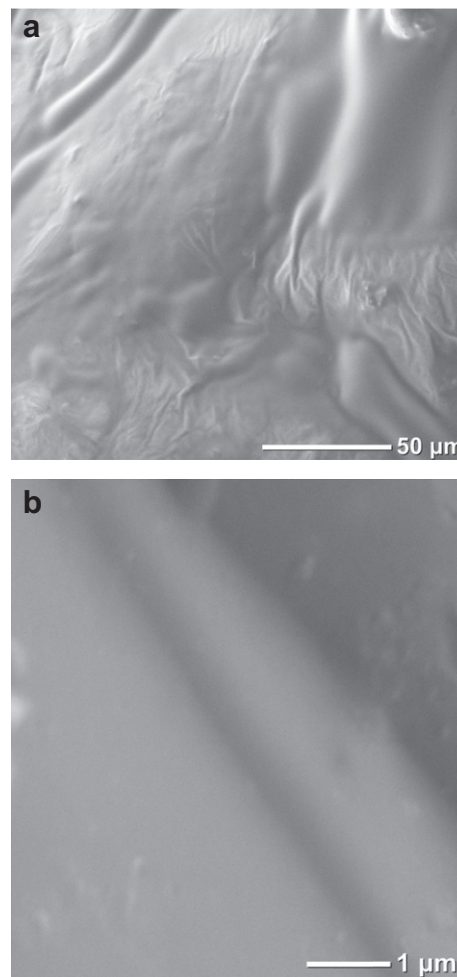


Fig. 4. SEM micrographs of the surface of PVPATS composite membranes (a) 50 μm (b) 1 μm

3.4. Thermal analysis

Table 1 lists the glass transition temperatures of the PVPATS_x nanocomposites. PVPA exhibits a glass transition at around $-23\text{ }^{\circ}\text{C}$ [42]. PVPATS_x nanocomposite polymer membranes have definite glass transition temperatures between $84\text{ }^{\circ}\text{C}$ and $100\text{ }^{\circ}\text{C}$. The results indicate that the glass transition temperatures of the samples shift to higher temperatures as the quantity of sulfated nano-titania increases. The reason can be attributed to inhibition of segmental relaxations due to complexation.

Fig. 5 shows the thermogravimetry (TG) results of the composite membranes under inert conditions. The TG graphs show an elusive weight loss up to $150\text{ }^{\circ}\text{C}$ which can be attributed to anhydride formation [42]. It is clear that the dried polymers are thermally stable up to $200\text{ }^{\circ}\text{C}$, then they decompose. As the nanoparticle content increases, the degradation temperature slightly shifts to higher temperature which may be due to inhibition of anhydride formation.

3.5. Conductivity measurement

The AC conductivities, $\sigma_{ac}(\omega)$ of the polymers were studied several temperatures using an impedance analyzer. The frequency dependent AC conductivities ($\sigma_{ac}(\omega)$) were measured using Eq. (1);

$$\sigma'(\omega) = \sigma_{ac}(\omega) = \epsilon''(\omega)\omega\epsilon_0 \quad (1)$$

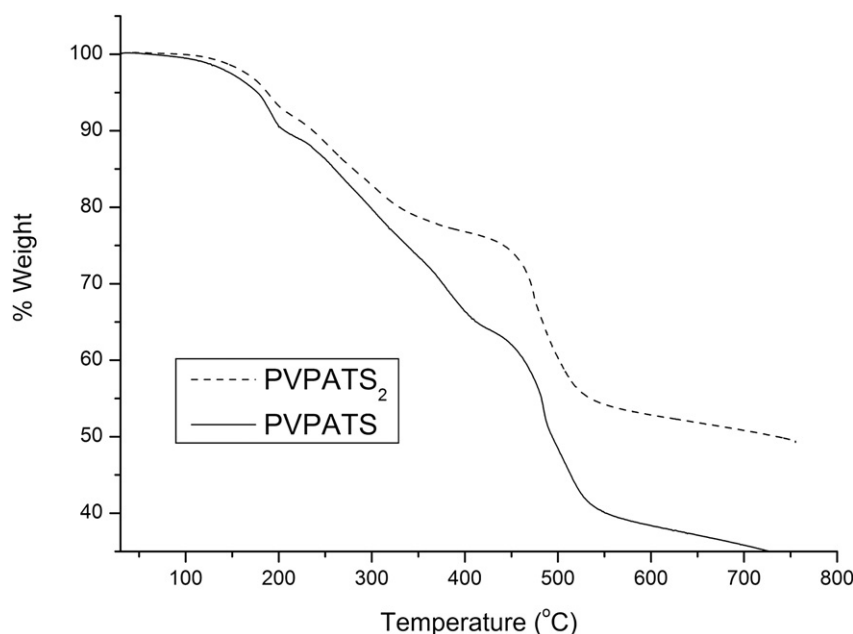


Fig. 5. Thermogravimetry (T_g) Analysis of PVPATS composite membranes under nitrogen atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$.

where $\sigma'(\omega)$ is the real part of conductivity, $\omega = 2\pi f$ is the angular frequency, ϵ_0 is the vacuum permittivity and ϵ'' is the imaginary part of complex dielectric permittivity (ϵ^*). The proton conductivities of PVPATS_x anhydrous nanocomposite polymer electrolytes were measured between 20 and 150°C . The AC conductivity of PVPATS_x composite membrane is shown in Fig. 6.

The proton conductivities of all anhydrous samples were compared in Fig. 7. The conductivity isotherm illustrates that the DC conductivity strongly depends on temperature as well as the ratio of PVPA.

The relation between self-condensation and proton conductivity of PVPA was investigated by Kaltbeitzel et al. [43]. Maximum proton conductivity for pristine PVPA was reached under 1 bar H_2O atmosphere. The proton conductivities of Nafion 117 membrane were ranging from 0.11 S cm^{-1} at room temperature to 0.20 S cm^{-1}

at elevated temperatures when the membrane was fully hydrated. The proton conductivity of Nafion 117 at 50% relative humidity was approximately 0.03 S cm^{-1} at 40°C [44–46].

Previously, Wu et al. have reported organophosphorylated titania and chitosan composite membranes which exhibit an increased proton conductivity of 0.01 S cm^{-1} (RH = 80%) for DMFC [38]. These organophosphorylated titania nanoparticles were enhanced the proton conductivity when they dispersed in the membranes at low temperatures in humidified conditions.

The proton conductivities of these samples increase with PVPA content and increasing temperature. The maximum proton conductivity was measured for PVPATS_x and found to be 0.03 S cm^{-1} at 150°C in the dry state. The material with $x = 1$ was considered to be the optimum composition as the complex polymer electrolyte. Conductivity results showed that the PVPA composition

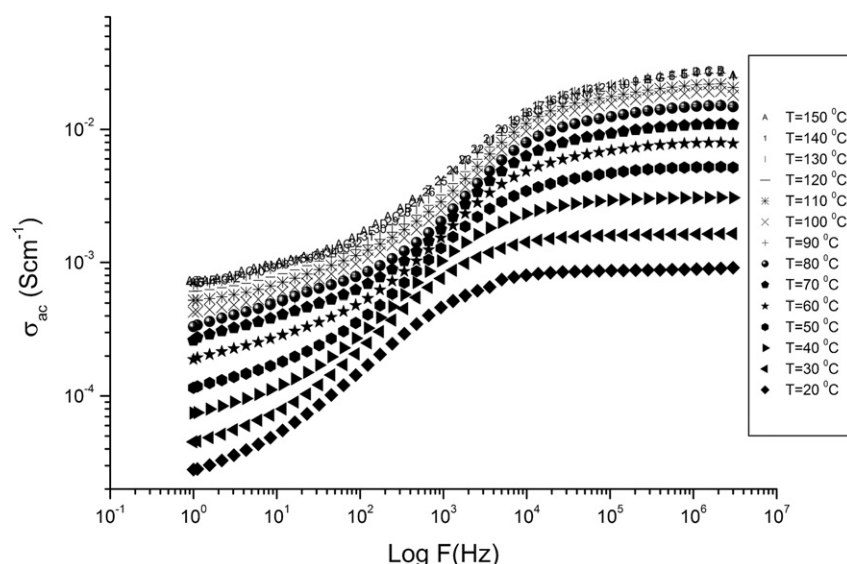


Fig. 6. AC Conductivity of PVPATS composite membranes.

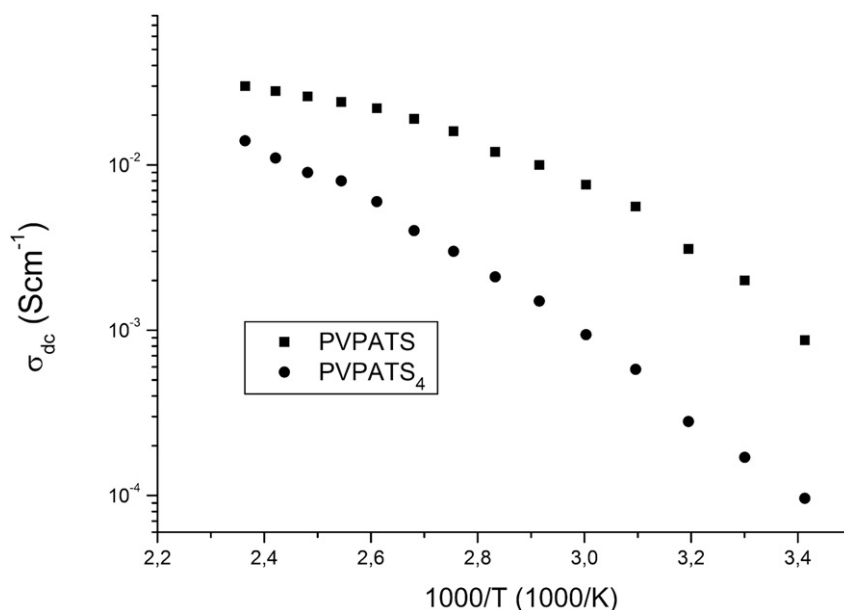


Fig. 7. DC Conductivity Measurements of PVPATS composite membranes versus reciprocal temperature.

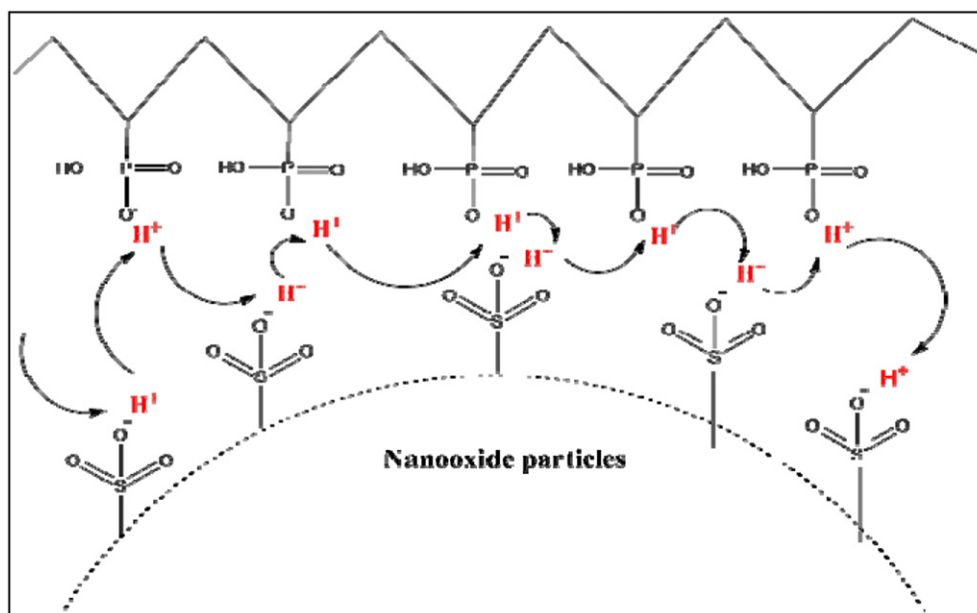


Fig. 8. Proton transfer mechanism in PVPATS composite membranes.

is highly effective on the proton conductivity of the samples in the PVPATS_x systems. The major part of proton transport is provided over both phosphonic acid coordinated with sulfated nano-titania. Previously, the structure and the local proton transport of the host matrix, PVPA were studied by solid-state NMR [47].

In the current system, proton transfer can be facilitated by the additional sulfated groups on titania fillers. From the FT-IR, composite membranes as well as conductivity data, it can be concluded that a Grotthuss mechanism (structural diffusion) is the possible pathway for the total proton diffusion. This continuous pathway may convey proton mobility over the –POH groups and sulfate groups may reduce the energy barrier for proton transport (Fig. 8). The proton could travel along the ionic bonds from one functional group to another [48,49].

4. Conclusions

In the present work, composite membranes from sulfated nano-titania and PVPA were produced. FT-IR spectroscopy confirmed the existence of complexation between the modified inorganic nano-particle and host polymer matrix. TG analysis showed that sulfated nano-titania inhibited anhydride formation increasing the thermal stability up to approximately 200 °C. DSC results illustrated that the *T_g* of the materials shifted to higher temperatures with increasing sulfated nano-titania ratio due to complexation. In the anhydrous state, the proton conductivity of PVPATS_x was found to be 0.03 S cm⁻¹ at 150 °C. In dried samples, the proton diffusion is expected to occur by the transport of the protons through phosphonic acid units up to certain threshold composition of PVPA. The

synthesized nanocomposite polymers can be suggested for application in polymer electrolyte membrane fuel cells (PEMFC).

Acknowledgments

This work was supported by Fatih University Research Foundation under the contract number P50021005_G.

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